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(54) Modified Epoxy Resins

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NO DRAWING

p4, fig 1-3
p5, fig 4
p6, fig 5-7
p30, fig 8-17



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Modified epoxy resins

{ The present invention relates to combinations of selected diene copolymers and capped urethane prepolymers, to mixtures comprising these combinations and epoxy resins, to the cured products obtainable from these mixtures and to the use of these mixtures as adhesives or sealants, in particular as structural adhesives.

DE-A-2,152,606 discloses mixtures of epoxy resins with phenol-capped polyurethanes. The polyurethanes are obtained by reacting prepolymeric diisocyanates with substituted or unsubstituted monophenols. The mixtures may be used in conjunction with polyamine curing agents for the preparation of coatings distinguished by a particularly high elasticity.

EP-A-66,167 discloses a process for the preparation of oligourethanes terminated by mercapto groups. These oligomers may be employed as binders for oxidatively curable coatings and sealants or as a elasticity-promoting additive for epoxy resins.

EP-A-231,760 discloses selected oligourethanes containing terminal mercapto groups. The compounds are derived from selected polyalkylene ethers and may be used as sealants or as additives to crosslinkable epoxy resins.

Finally, EP-A-30,426 discloses liquid compositions containing two oligomers of different reactivities which are mutually compatible and are each independently curable. They may also be, inter alia, mixtures of a butadiene/acrylonitrile copolymer containing reactive terminal groups with an isocyanate-terminated prepolymer. These mixtures may additionally comprise a component, for example an epoxy resin, which reacts with at least one of the liquid oligomers and becomes unblocked in the curing.



It is furthermore known that epoxy resins may be modified by the addition of copolymers based on butadiene/acrylonitrile or by the addition of adducts of such copolymers to epoxy resins.

The previously disclosed modified epoxy resins generally possess after curing high impact strength and flexibility. The peel strength, however, usually leaves much to be desired. Moreover, the lap shear strength and glass transition temperature of the cured mixtures are lowered compared with the cured non-modified epoxy resins.

Combinations of impact strength modifiers have been found which produce in admixture with epoxy resins a significant rise in peel strength and a reduced tendency to crack propagation, and promote high peel strengths without loss of lap shear strength.

Furthermore, using these modifiers it is possible to produce elastic products of high peel strength and low glass transition temperature or high-strength products of high glass transition temperature and high peel strength, depending on the resin formulation; the high-strength products are distinguished by high fracture toughness, and crack propagation is distinctly reduced even at high impact load, similar to shock.

The present invention relates to compositions comprising

A) a liquid copolymer based on butadiene, a polar, ethylenically unsaturated comonomer and a further non-polar ethylenically unsaturated comonomer, the said copolymer containing optional terminal groups reactive toward epoxy resins, or an adduct of said liquid copolymer with an epoxy resin via the said terminal groups, and

B) a compound of the formula I



in which m is 2 to 6, R^1 is the m-valent radical of an elastomeric prepolymer, after removal of the terminal isocyanate, amino or hydroxyl groups, which is soluble or dispersible in epoxy resin, X is -O- or

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-NR²-, where R² is hydrogen, C₁-C₆alkyl or phenyl, Y is -O-, R³ is the radical of a monophenol or of an aliphatic or cycloaliphatic mercapto-alcohol after removal of one hydroxyl group, or Y and R³ form jointly the radical of an aliphatic lactam which is attached to the carbonyl group via the N atom, with the proviso that at least one of the groups -X- or -Y-R³ contain a nitrogen atom.

The component A) is a selected liquid elastomeric copolymer based on butadiene and preferably contains terminal groups reactive toward epoxy resins.

This component may be used as such or as an adduct with an epoxy resin, preferably a diglycidyl ether based on bisphenol.

Within the scope of this description, the expression "liquid copolymer" is understood to refer to a compound which is free-flowing at temperatures below 80°C and is readily miscible with an epoxy resin.

Examples of polar, ethylenically unsaturated comonomers for the preparation of the component A) are acrylic acid, methacrylic acid, esters of acrylic or methacrylic acid, for example the methyl or ethyl esters, amides of acrylic or methacrylic acid, fumaric acid, itaconic acid, maleic acid or their esters or hemi-esters, for example mono- or dimethyl esters, or maleic or itaconic anhydride; vinyl esters, for example vinyl acetate, polar styrenes, such as styrenes chlorinated or brominated in the nucleus, or particularly acrylonitrile or methacrylonitrile.

In addition to polar, ethylenically unsaturated comonomers, the component A) may also contain further non-polar, ethylenically unsaturated comonomers. Examples of these are ethylene, propylene or in particular styrene or substituted styrenes, such as vinyltoluene.

Component A) may be a statistical copolymer, a block copolymer or a graft copolymer.

The amount of the comonomers in the component A) may fluctuate within a wide range. This component is selected in such a manner that an elastomeric phase forms in combination with the component B) and, if desired, an epoxy resin C). The system may be either a homogeneous or a heterogeneous one.

An elastomeric phase may already be present in the component A), for example if a polybutadiene graft copolymer is used; however, the elastomeric phase may also result simply from selecting suitable components A), B) and, if desired, C).

If heterogeneous systems are required, the components are usually selected in such a manner that the difference of the solubility parameters of A) and/or B) on the one hand and C) on the other is between 0.2 and 1.0, preferably between 0.2 and 0.6. The selection criteria are described, for example, in chapter 2 of "Toughened Plastics" by C.B. Bucknall, Applied Science Publishers Ltd., London 1977.

The components A) which are preferred, are liquid copolymers based on butadiene-acrylonitrile, butadiene-acrylonitrile-styrene graft copolymers (ABS) and butadiene-methyl methacrylate-styrene graft copolymers (MBS).

The components A) which are particularly preferred, are liquid copolymers obtainable by graft copolymerization of polar, ethylenically unsaturated comonomers onto polybutadiene microgels.

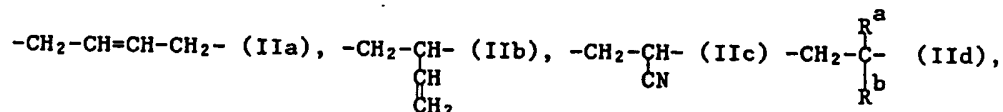
Liquid butadiene-acrylonitrile copolymers are the components A) most particularly preferred.

The molecular weights of these preferred components A) are preferably 500-5000, in particular 1000-3000.

Other particularly preferred components A) are butadiene-acrylonitrile copolymers containing functional groups reactive toward epoxy resins.

Examples of such copolymers are the acrylonitrile-butadiene rubbers containing carboxyl or hydroxyl or amino groups, for example compounds of the type Hycar® from Goodrich.

The preferred types of such rubbers comprise structural elements of the following formulae IIa to IId and the terminal groups Q



where R^a is hydrogen or methyl, R^b is $-\text{COOH}$, $-\text{COOR}^c$ or $-\text{CONH}_2$, R^c is an aliphatic radical, preferably methyl, and Q is selected from the group

consisting of $-\text{R}-\text{COOH}$, $-\text{R}-\text{OH}$ and $-\text{R}-\text{CO}-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \cdot \quad \cdot \end{array} \text{NH}$, in which R is an

alkylene radical; the amount of the radicals IIa and IIb is preferably 5-50 % by weight, the amount of the radical Ic is preferably 5-50 % by weight, the amount of the radical IIId is preferably 0-30 % by weight but preferably 0-10 % by weight if the radicals contain free carboxyl groups, the amounts being based on the total amounts of the radicals IIa, IIb, IIc and IIId if any.

The component A) is preferably used in the form of an adduct of a butadiene-acrylonitrile copolymer containing functional groups reactive toward epoxy resins with an epoxy resin.

The preparation of such adducts is carried out in a manner known per se by heating the reactive acrylonitrile-butadiene rubber and the epoxy resin, if desired in the presence of a catalyst, so that a fusible precondensate results, which however may still be cured.

Examples of a catalyst are triphenylphosphine, tertiary amines, quaternary ammonium or phosphonium salts or chromium acetylacetonate.

The component B) is a selected polyurethane or a selected polyurea. These compounds are derived from specified prepolymers and contain specific terminal groups attached via urethane or urea groups.

Within the scope of this description, the expression "elastomeric prepolymer radical R¹" is understood to refer to a radical containing terminal m-isocyanate, amino or hydroxyl groups of a prepolymer which after capping of these groups gives rise to a compound of the formula I which yields in combination with the diene component A) and the epoxy resins C) after curing an elastomeric phase or a mixture of elastomeric phases, in which case the combinations of the components A), B) and C) may be homogeneous or preferably heterogeneous. The elastomeric phase or phases is or are usually characterized by a glass transition temperature of less than 0°C.

Within the scope of this description, the expression "prepolymer soluble or dispersible in epoxy resins" is understood to refer to a radical containing terminal m-isocyanate, amino or hydroxyl groups of a prepolymer which after capping of these groups gives rise to a compound of the formula I which is soluble or dispersible without any further auxiliary agents, for example emulsifiers, in an epoxy resin C) or in a combination of an epoxy resin C) and a butadiene copolymer A), a homogeneous phase forming at the same time or at least no macroscopic phase separation of one of the components A), B) or C) or of a mixture of the said components taking place.

In the case of heterogeneous systems the difference of the solubility parameters of A) and/or B) and/or C), described above, should usually be maintained.

The solubility or dispersibility of B) in the combination of A) and C) is achieved in particular by the choice of suitable prepolymer radicals R¹. Examples of suitable radicals are given below under preparation of the component B).

The component B) is preferably a water-insoluble compound of the formula I. Within the scope of this description this is understood to be a compound which dissolves in water to a lesser extent than 5 % by

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weight, preferably to a lesser extent than 1 % by weight, and which on storage in water takes up only a small amount of water, preferably less than 5 % by weight, or under those conditions swells only slightly.

The prepolymers forming the basis of the radical R^1 usually have molecular weights (number average) of 150 to 10,000, preferably 500 to 3000.

The average functionality of these prepolymers is at least 2, preferably 2 to 3, and particularly preferably 2 to 2.5.

The expression "elastomeric polyurethane" or "elastomeric polyurea" is known per se to the person skilled in the art (cf. C. Hepburn: "Polyurethane Elastomers", Applied Science Publishers, London 1982).

Elastomeric polyurethanes or polyureas generally contain rigid and flexible components (hard and soft segments).

The component B) may be either a liquid or a thermoplastic compound of the formula I. Compounds having a softening point below 80°C, preferably below 40°C, are preferred.

Suitable components B) may essentially be linear or they may be of the branched type. In the latter case the degree of branching is chosen such that the solubility or dispersibility of the component in question in the components A) and C) is defined. This will be usually so if the component B) is soluble or dispersible in a polar organic solvent or in an epoxy resin.

The compounds of the formula I may be obtained in a variety of ways depending on the nature of the basic prepolymer or on the meaning of the groups X and Y.

Compounds of the formula I where X is $-NR^2-$ and Y is $-O-$ or where Y and R^3 form jointly the radical of an aliphatic lactam, may be prepared for

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example by reacting prepolymeric isocyanates of the formula IIIa with H-acid compounds of the formula IVa (method a)



polyureas of the formula I may be further prepared by reacting prepolymeric amines of the formula IIIb with urethanes of the formula IVb (method b)



compounds of the formula I in which X is -O- and Y and R³ form jointly the radical of an aliphatic lactam, may be prepared by reacting prepolymeric alcohols of the formula IIIc with urethanes of the formula IVb (method c)



compounds of the formula I, in which X is -O- and Y and R³ form jointly the radical of an aliphatic lactam, may be further prepared by reacting chlorocarbonyloxy derivatives of the formula IIId with H-acid compounds of the formula IVd (method d)



in these formulae IIIa to IIId and IVa to IVd, R¹, R², R³, X, Y and m are as defined above, R⁴ and R⁵ form jointly with the nitrogen atom they have in common the radical of an aliphatic lactam, and R⁶ is a radical functioning as a leaving group, for example alkyl or aryl, in particular C₁-C₆alkyl or phenyl.

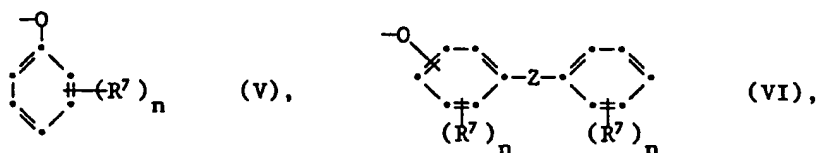
The radical R³ is derived from a selected OH-acid or NH-acid component. R³ is usually unsubstituted or the radical carries inert substituents; examples of these are alkyl, alkenyl, alkynyl, alkoxycarbonyl, alkoxy or halogen.

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A radical R^3 derived from a monophenol is preferably a mononuclear or polynuclear carbocyclic-aromatic radical. Polynuclear radicals may be condensed. Dinuclear radicals are preferably attached to each other via a bridging link. Examples of bridging link are given below.

Examples of phenols with condensed radicals are hydroxynaphthalenes or hydroxyanthracenes.

Where R^3 is derived from a monophenol, then the group $-Y-R^3$ has preferably the structure of the formula V or VI



in which R^7 is C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyl, C_2 - C_6 alkynyl, $-CO-OR^8$ or halogen, n is 0, 1 or 2, Z is a direct C-C bond or a bridging link selected from the group consisting of $-CR^9R^{10}-$, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-COO-$, $-CONR^{11}-$ and $-SiR^{12}R^{13}-$, R^9 , R^{10} and R^{11} independently of one another are hydrogen, $-CF_3$ or C_1 - C_6 alkyl, or R^9 and R^{10} form jointly with the carbon atom they have in common a cycloaliphatic radical having 5 to 12 carbon atoms, R^8 is C_1 - C_{20} alkyl and R^{12} and R^{13} are C_1 - C_6 alkyl.

The phenolic radicals of the formulae V or VI in which n is 0 or 1 and R^7 is C_1 - C_6 alkyl, allyl, prop-1-enyl or C_1 - C_6 alkoxy, are particularly preferred.

The phenolic radicals of the formula VI in which the free valency is located at the 4 position to the bridge Z , are most particularly preferred.

Further preferred radicals are those of the formula VI in which Z is selected from the group consisting of $-CH_2-$, $-C(CF_3)_2-$, $-O-$, $-SO_2-$, a direct C-C bond and particularly $-C(CH_3)_2-$, and in which n is 0.

Preferred monophenols are phenol, o-, m- or p-cresol, 4-hydroxybiphenyl, 4-hydroxyphenoxybenzene, 4-hydroxyphenylsulfonylbenzene, 4-hydroxyphenylmethylbenzene or alkyl 4-hydroxybenzoate, for example the methyl or nonyl ester.

A C_1-C_{20} alkyl or C_1-C_{20} alkoxy radical R^7 or a C_1-C_{20} alkyl radical R^8 are straight-chain or branched radicals.

Examples of these are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, 2-ethylbutyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-octadecyl or n-eicosyl or their corresponding alkoxy derivatives.

R^7 is preferably C_1-C_6 alkyl or C_1-C_6 alkoxy, particularly preferably straight-chain C_1-C_6 alkyl or C_1-C_6 alkoxy and most preferably methyl or methoxy.

Any C_1-C_6 alkyl radical is for example preferably a straight-chain radical, i.e. methyl, ethyl, n-propyl, n-butyl, n-pentyl or n-hexyl, most particularly however methyl.

A C_2-C_{20} alkenyl radical R^7 is for example vinyl, allyl, 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, pentadec-8-enyl, pentadec-8,11-dienyl or pentadec-8,11,14-trienyl. Vinyl, 1-propenyl and allyl are preferred, allyl most particularly so.

A C_2-C_6 alkynyl radical R^7 is for example ethynyl, propargyl, 1-butyne, 1-pentyne or 1-hexyne, propargyl being preferred.

A halogen radical R^7 is for example fluorine, chlorine, bromine or iodine. Chlorine or bromine are preferred, bromine particularly so.

The radicals R^9 and R^{10} which form jointly with the carbon atom they have in common a cycloaliphatic radical are for example a cyclopentylidene,

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cyclohexylidene, cycloheptylidene, cyclooctylidene or cyclododecylidene radical. Cyclohexylidene and cyclododecylidene radicals are preferred.

Where Y and R³ form jointly the radical of an aliphatic lactam, the group -Y-R³ is usually a lactam formed from an aliphatic γ-, δ- or ε-amino-carboxylic acid; in particular a radical of the formula VII



in which p is 3 to 5.

Radicals of the formula VII where p is 5, are preferred.

Where R³ is derived from an aliphatic or cycloaliphatic mercaptoalcohol, the group -Y-R³ is usually a radical of the formula VIII



in which R¹⁴ is C₂-C₁₂alkylene or cycloalkylene having 5 to 7 cyclic carbon atoms.

If desired, the radicals R¹⁴ may be substituted by one to three alkyl or alkoxy groups or they may be interrupted in the alkylene chain by oxygen or sulfur atoms.

Examples of alkylene radicals R¹⁴ are ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, undecamethylene, dodecamethylene,

-(CH₂-CH₂-O)₂-CH₂-CH₂-, -(CH(CH₃)-CH₂-O)₂-C(CH₃)-CH₂- or

-(CH₂-CH₂-CH₂-CH₂-O)₂-CH₂-CH₂-CH₂-CH₂-.

Examples of cycloalkylene radicals R¹⁴ are cyclopentylene, cyclohexylene, cycloheptylene or methylcyclohexylene. Ethylene is the preferred radical R¹⁴.

The isocyanate of the formula IIIa is either a prepolymer al) which is derived from an addition of a polyisocyanate, preferably a di- or triisocyanate, most particularly preferably of a diisocyanate, to a

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prepolymeric polyhydroxyl or polysulfhydryl component or to a mixture of such prepolymeric components, if desired in combination with chain extenders (short-chain polyhydroxyl, polysulfhydryl or polyamine compounds), or it is a prepolymeric polyisocyanate a2) which is derived from a prepolymeric polyamine of the formula IIIb, particularly from a prepolymeric polyether amine.

Prepolymeric components for the preparation of a1) may be condensation or addition polymers which may, if desired, contain grafted 1-olefins, it being possible for the said 1-olefins to comprise, in addition to non-polar groups, also polar groups such as nitrile, ester or amide groups. Examples of such prepolymers are polyesters, polyethers, polythioethers, polyacetals, polyamides, polyester amides, polyurethanes, polyureas, alkyd resins, polycarbonates or polysiloxanes, provided that these compounds are terminated in hydroxyl or sulfhydryl, give rise to compounds of the formula I which are soluble or dispersible in epoxy resins and impart to the said compounds elastomeric properties as defined above.

Polyethers or polyether segments containing segmented prepolymers such as polyether amides, polyether urethanes or polyether ureas, are preferred.

These compounds are known to a person skilled in the field of polyurethane chemistry as components for the synthesis of polyurethanes. They may be linear or branched, the linear type being preferred. Preferred synthesis components for the prepolymers a1) are hydroxyl-terminated prepolymers having an average molecular weight (number average) of 150-10,000, most particularly of 500-3000.

In the preparation of the prepolymeric polyisocyanates a1) chain extenders may be also present in addition to hydroxyl- or sulfhydryl-terminated prepolymers.

Such monomers are preferably difunctional or trifunctional.

If tri- or higher-functional hydroxyl- or sulfhydryl-terminated prepolymers or tri- or higher-functional chain extenders are used for the preparation of the component a1), the synthesis components are to be chosen such that an adduct a1) is formed which is soluble, or at least capable of swelling, in organic solvents.

If higher-functional synthesis components are used, it is possible to control the degree of crosslinking in a manner known per se by the nature and amounts of these components. The elastomeric properties may also be varied in a manner known per se by the degree of crosslinking.

Thus, if difunctional prepolymers and tri- or higher-functional chain extenders are employed, only a small amount of the higher-functional component is usually used, while with a combination of di- and tri- or higher-functional prepolymers a greater amount of the higher-functional chain extender can usually be present without any excessive crosslinking taking place. Furthermore the degree of crosslinking also depends on the functionality of the polyisocyanate. Thus diisocyanates are usually used in the presence of tri- or higher-functional hydroxyl- or sulfhydryl-terminated synthesis components, while if difunctional hydroxyl- or sulfhydryl-terminated synthesis components are used, higher-functional isocyanates are also employed. Examples of prepolymeric synthesis components for the preparation of polyisocyanates a1) are hydroxyl-terminated polyethers, in particular such polyethers which give rise to water-insoluble compounds of the formula I.

Examples of such polyethers are the polyalkylene ether polyols which may be obtained by anionic polymerization, copolymerization or block copolymerization of alkylene oxides such as ethylene oxide, propylene oxide or butylene oxide, with di- or polyfunctional alcohols such as 1,4-butanediol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 1,2,6-hexanetriol, glycerol, pentaerythritol or sorbitol, or with amines such as methylamine, ethylenediamine or 1,6-hexylenediamine, as initiation components, or by cationic polymerization or copolymerization of cyclic ethers such as tetrahydrofuran, ethylene oxide or propylene oxide in the presence of acid catalysts such as boron trifluoride etherate, or by

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polycondensation of glycols capable of polycondensation with elimination of water, such as 1,6-hexanediol, in the presence of acid etherification catalysts such as p-toluenesulfonic acid. In addition oxalkylation products of phosphoric acid or phosphorous acid with ethylene oxide, propylene oxide, butylene oxide or styrene oxide may be used.

Further preferred hydroxyl-terminated polyethers contain grafted 1-olefins such as acrylonitrile, styrene or acrylic acid esters, in which case the weight of the graft components usually amounts to 10-50 %, in particular 10-30 %, based on the amount of the polyether employed.

Other examples of prepolymeric synthesis components for the preparation of polyisocyanates a1) are hydroxyl-terminated polyester polyols derived from dicarboxylic and/or polycarboxylic acids and diols and/or polyols, preferably from dicarboxylic acids and diols.

Examples of such polycondensates are hydroxyl-terminated polyesters which may be obtained by polycondensation of adipic acid, sebacic acid, azelaic acid, dimeric and trimeric fatty acids, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid and endomethylenetetrahydrophthalic acid with propylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene, triethylene and tetraethylene glycol, dipropylene, tripropylene and tetrapropylene glycol, dibutylene, tributylene and tetrabutylene glycol, 2,2-dimethylpropane-1,3-diol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane and 1,2,6-hexanetriol.

Other suitable prepolymeric synthesis components for the preparation of the polyisocyanates a1) are hydroxyl-terminated polybutadienes which are used in particular in conjunction with hydroxyl-terminated polyethers to form the component a1).

Further examples of suitable prepolymeric synthesis components for the preparation of the polyisocyanates a1) are polymerization products of lactones, for example ϵ -caprolactones; or polyalkylene thioether polyols,

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for example polycondensation products of the thiodiglycol with itself and with diols and/or polyols, for example 1,6-hexanediol, triethylene glycol, 2,2-dimethyl-1,3-propanediol or 1,1,1-trimethylolpropane. Hydroxyl-terminated polyethers or polyesters are the preferred prepolymeric synthesis components for the preparation of the polyisocyanates a1).

Other preferred prepolymeric synthesis components for the preparation of the polyisocyanate a1) are mixtures of hydroxyl-terminated polybutadiene and hydroxyl-terminated polyalkylene glycol or hydroxyl-terminated polyalkylene glycols comprising grafted 1-olefins, in particular styrene or acrylic acid derivatives such as acrylic acid esters or acrylonitrile.

Hydroxyl-terminated polyethers, particularly dihydroxyl-terminated polyalkylene glycols, are the most particularly preferred prepolymeric synthesis components for the preparation of the polyisocyanates a1).

Chain extenders for the preparation of the prepolymeric synthesis components a1) are known per se. Examples of these are the diols and polyols for the preparation of the hydroxyl-terminated polyethers already referred to above, particularly the diols and triols such as 1,4-butanediol, 1,1,1-trimethylolpropane or hydroquinone (2-hydroxyethyl ether), or likewise diamines such as diaminoethane, 1,6-diaminohexane, piperazine, 2,5-dimethylpiperazine, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane, 4,4'-diaminocyclohexylmethane, 1,4-diaminocyclohexane and 1,2-propylene-diamine or also hydrazine, amino acid hydrazides, hydrazides of semicarbazidocarboxylic acids, bis-hydrazides and bis-semicarbazides.

Short-chain diols or triols are preferably used as chain extenders.

The prepolymeric polyisocyanate a2) may be obtained in a manner known per se from amino-terminated prepolymers of the formula IIb, in particular from amino-terminated polyethers by reaction with phosgene or with polyisocyanates, preferably with diisocyanates or triisocyanates, particularly preferably with diisocyanates. Apart from the amino groups, the amino-terminated prepolymers generally contain no other radicals con-

taining active hydrogen atoms. Prepolymers with terminal amino groups are generally derived from the hydroxyl-terminated condensation or addition polymers described above as synthesis component for a1), particularly from polyethers.

They may be obtained by reacting the said condensation or addition polymers containing secondary hydroxyl groups with ammonia or by reacting the said condensation or addition polymers containing primary hydroxyl groups, for example polybutylene glycol, with acrylonitrile, and by subsequently hydrogenating these products.

Prepolymeric, isocyanate-terminated polyTHF may be also obtained according to S. Smith et al. in Macromol. Sci. Chem., A7(7), 1399-1413 (1973) by interrupting a difunctional live cationic THF polymer with potassium cyanate.

Aliphatic, cycloaliphatic, aromatic or araliphatic di-, tri- or tetraiso-cyanates or precursors convertible to such isocyanates are usually used as the polyisocyanate for the preparation of the components a1) or a2).

The aliphatic, cycloaliphatic or araliphatic di- or triisocyanates are preferred and most particularly so the aliphatic or cycloaliphatic diisocyanates.

The preferred aliphatic diisocyanates are usually straight-chain or branched alkylene α,ω -diisocyanates. If desired, the alkylene chains may be interrupted by oxygen or sulfur atoms and, if desired, may contain ethylentically unsaturated bonds.

α,ω -Diisocyanates having straight-chain, saturated C_2 - C_{12} alkylene radicals are preferred.

Examples of such radicals have already been given above for R¹⁴.

The preferred cycloaliphatic diisocyanates are usually derivatives derived from substituted or unsubstituted cyclopentanes, cyclohexanes or

cycloheptanes. Two such rings may also be joined together by a bridging link.

Examples of such radicals are 1,3- and 1,4-cyclohexylene or dodecahydro-diphenylmethane-4,4'-diyl.

Diisocyanates or triisocyanates derived from dimeric or trimeric fatty acids may be further used. These compounds may be prepared in a manner known per se from the fatty acids by a rearrangement to the corresponding diisocyanates or triisocyanates (Hoffmann, Curtius or Lossen rearrangements).

Preferred aromatic diisocyanates are derived from mononuclear or dinuclear aromatic radicals. They possess for example the structures V or VI in which the phenolic OH group is replaced by a NCO group and where a second NCO group is linked to the aromatic nucleus.

Examples of aromatic diisocyanate radicals are 1,2-, 1,3- or 1,4-phenylene or 4,4'-diphenylmethane.

Examples of araliphatic diisocyanate radicals are 1,2- and 1,4-xylylene.

Specific examples of suitable polyisocyanates are 2,4-diisocyanatotoluene and its technical mixtures with 2,6-diisocyanatotoluene; 2,6-diisocyanatotoluene, 1,5-diisocyanatonaphthalene, 4,4'-diisocyanatodiphenylmethane and technical mixtures of various diisocyanatodiphenylmethanes (for example the 4,4' and 2,4' isomers), urethanized 4,4'-diisocyanatodiphenylmethane, carbodiimidized 4,4'-diisocyanatodiphenylmethane, the urethdione of the 2,4-diisocyanatotoluene, triisocyanatotriphenylmethane, the adduct from diisocyanatotoluene and trimethylolpropane, the trimer from diisocyanatotoluene, diisocyanato-m-xylylene, N,N'-di(4-methyl-3-isocyanatophenyl)urea, mixed trimerization products from diisocyanatotoluene and 1,6-diisocyanatohexamethylene, 1,6-diisocyanatohexane, 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (isophorone diisocyanate), N,N',N''-tri(6-isocyanatohexyl)biuret, 2,2,4-trimethyl-1,6-diisocyanatohexane, 1-methyl-2,4-diisocyanatocyclohexane, dimeryl-

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diisocyanate, 4,4'-diisocyanatodicyclohexylmethane, trimeric isophorone diisocyanate, trimeric hexane diisocyanate and methyl 2,6-diisocyanatohexanoate.

The preparation of the components a1) or a2) is carried out in a manner known per se by reacting the hydroxyl-, sulfhydryl- or amino-terminated elastomeric prepolymer component with a polyisocyanate or a mixture of these components. If desired, the reactions may be performed in the presence of a chain extender.

The preparation of the component a1) or a2) is carried out without solvents or in solvents which are inert to isocyanates.

Examples of inert solvents are esters such as ethyl acetate, butyl acetate, methyl glycol acetate and ethyl glycol acetate; ketones such as methyl ethyl ketone or methyl isobutyl ketone; aromatic hydrocarbons such as toluene or xylene or halogenated hydrocarbons such as trichloroethane or methylene chloride.

If a certain additional chain extending reaction via urethane or urea groups is acceptable or even desirable, then the prepolymers containing hydroxyl, sulfhydryl or amino groups and any monomers which may be present are reacted with the diisocyanate or polyisocyanate first, if desired, at 0-25°C with cooling and later, if desired, with heating for several hours to preferably 50-120°C, at a NCO/OH or NCO/SH or NCO/NH₂ ratio of 1.5-2.5, preferably 1.8-2.2.

If a chain extending reaction is not desired, a substantially greater excess of diisocyanate or polyisocyanate is usually employed, for example an NCO/OH, NCO/SH or NCO/NH₂ ratio of 3-5, and no chain extender and otherwise the procedure described for the lower NCO/OH, NCO/SH or NCO/NH₂ ratios is followed. If desired, the excess diisocyanate or polyisocyanate is removed after the reaction, for example by thin-layer distillation or by solvent extraction.

The reaction of the hydroxyl-, sulfhydryl- or amino-terminated pre-polymers with polyisocyanates is carried out in the presence of catalysts known per se.

Examples of such catalysts are diazabicyclooctane, dibutyltin dilaurate or tin-II octoate. These catalysts are used in conventional amounts, for example in amounts from 0.001-2 % by weight based on the amount of polyisocyanate.

The reaction of the polyisocyanate IIIa with the H-acid component IVa is carried out as described above for the reaction of the hydroxyl-, sulfhydryl- or amino-terminated synthesis component with the polyisocyanate, in which case the H-acid component IVa is preferably introduced in such an amount that the free NCO groups are essentially used up in the reaction.

If compounds of the formula I, capped with phenol, are to be prepared, then it is possible to use also a mixture of one or more monophenols and a small amount of bisphenols as the H-acid component IVa. An example of such a mixture is cashew nut oil or nonylphenol/bisphenol A, in which case the amounts of the starting products IIIa and IVa are usually chosen such that a chain extension occurs via the bisphenol component and a derivative of the formula I, essentially capped with monophenol, results. However, it is also possible that small amounts of free phenolic hydroxyl groups occur in the mixture of the compounds of the formula I.

If an excess of phenol is used for the capping of the prepolymers then the free phenol usually is reacted with epoxy resins.

The reaction of the prepolymeric polyisocyanates IIIa with the mercapto-alcohols IVa is usually carried out in the presence of tin-containing catalysts such as dibutyltin dilaurate or tin-II octoate.

The amino-terminated prepolymers IIIb in the method b) and the hydroxyl-terminated prepolymers IIIc in the method c) are usually the prepolymeric polyamines and polyhydroxyl compounds which have already been described in the method a) and which are used therein for the preparation of the prepolymeric polyisocyanate components IIIa.

The prepolymeric chlorocarbonyloxy derivatives IIId in the method d) may be obtained from the hydroxyl-terminated prepolymers IIIc by reaction with phosgene.

The urethanes IVb are derived from lactams $H-NR^4-R^5$, wherein R^4 and R^5 are as defined above. To prepare these urethanes, these lactams are capped with $R^6-O-CO-Cl$ in a manner known per se, R^6 being as defined above.

The reaction of the components IIIb and IVb or IIIc and IVb or IIId and IVd is generally carried out using a stoichiometric ratio of the two components or a small excess of the component IVb or IVd and by heating the mixture, so that virtually all free reactive groups of the component IIIb, IIIc or IIId are capped. The reaction is preferably carried out in a solvent. Appropriate examples have been given above.

The molecular weight (number average) of the compounds of the formula I is usually in the range of 500-50,000, preferably in the range of 500-10,000, particularly preferably in the range of 500-3000.

The viscosity of these compounds is usually less than 150,000 mPas, preferably less than 100,000 mPas (measured at 80°C using an Epprecht viscometer).

The structures of the compounds of the formula I which are derived from the reaction according to the method a), b), c) or d), are differentiated according to the functionality of the prepolymeric radical R^1 .

In the method a) this functionality is determined, for example, by the functionality of the hydroxyl-, sulfhydryl- or amino-terminated pre-polymers, if desired by the chain extenders used, by the functionality of the isocyanate used for the preparation of IIIa and by the proportions of the individual reactants.

The compounds of the formula I in which X is -NH- and Y is -O- are the preferred components B).

Equally preferred components B) are compounds of the formula I which can be obtained by reacting

a) a prepolymeric polyisocyanate which

a1) is an adduct of a polyisocyanate with a prepolymeric polyhydroxyl or polysulfhydryl compound or with a mixture of such compounds, optional in combination with a chain extender, or

a2) is derived from a prepolymeric polyether amine, with

b) at least one monophenol.

Compounds of the formula I in which the component a1) is an adduct of a polyisocyanate with a hydroxyl-terminated prepolymer of an average molecular weight of 150 to 10,000, are particularly preferred.

Compounds of the formula I in which the synthesis component for the preparation of the component a1) is a hydroxyl-terminated polyether, are particularly preferred.

This synthesis component for the preparation of the component a1) is advantageously used in combination with chain extenders.

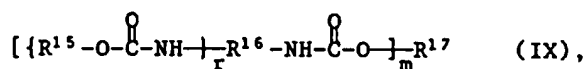
Compounds of the formula I in which the component b) is a mixture of a monophenol with a small amount of a bisphenol, particularly cashew nut oil, are most particularly preferred.

Compounds of the formula I in which the polyisocyanate for the preparation of the component a1) is an aliphatic, cycloaliphatic, aromatic or

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araliphatic diisocyanate or triisocyanate, are most particularly preferred.

In a preferred embodiment, the preparation of the component a) is carried out using a hydroxyl-terminated polyether or polyester, in the absence of a chain extender, and an amount of polyisocyanate which is equivalent to, or in excess of, the hydroxyl content; the isocyanate prepolymer is then capped with a monophenol, affording the polyurethanes of the formula IX



in which R^{15} is the radical of a monophenol after removal of the phenolic hydroxyl group, r is an integer between 1 and 3, R^{16} is the $r+1$ -valent radical of an aliphatic, cycloaliphatic, aromatic or araliphatic polyisocyanate after removal of the isocyanate groups, R^{17} is a m -valent hydroxyl-terminated polyester or polyether radical after removal of the terminal OH groups, with the proviso that the radicals R^{15} and R^{16} may be different within a given molecule.

Compositions containing compounds of the formula IX as the component B) are preferred.

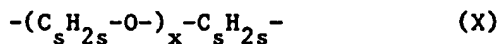
The index m is preferably 2 or 3, most particularly preferably 2. The index r is preferably 1.

Preferred components B) are compounds of the formula IX in which m is 2 or 3, r is 1, $-O-R^{15}$ is a radical of the formula V or VI, R^{16} is derived from an aliphatic, cycloaliphatic or aromatic diisocyanate and R^{17} is a divalent or trivalent radical of a hydroxyl-terminated polyester or polyether having a molecular weight of 150 to 10,000, in particular 500 to 10,000, after removal of the terminal hydroxyl groups.

Most particularly preferred components B) are compounds of the formula IX in which m is 2 or 3, r is 1, $-O-R^{15}$ is a radical of the formula V, R^{16} is derived from an aliphatic or cycloaliphatic diisocyanate and R^{17} is a divalent or trivalent radical of a polyalkylene ether polyol having a

molecular weight of 1000 to 3000 after removal of the terminal hydroxyl groups.

The particularly preferred components B) defined last comprise those wherein m is 2 and R¹⁷ is a structural element of the formula X



wherein s is 3 or 4, x is an integer of about 5 to 90 and the units -C_sH_{2s}-O- within a given structural element of the formula X may be different within the scope of the given definitions.

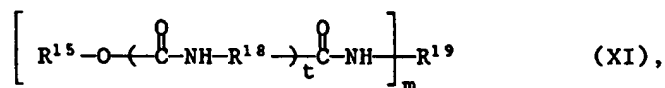
Examples of structural elements of the formula X are

-(CH₂-CH(CH₃)-O)_x-CH₂CH(CH₃)-, -(CH₂-CH₂-CH₂-CH₂-O)_x-CH₂CH₂CH₂-CH₂- as well as copolymers containing these structural elements.

Equally preferred components B) of this invention comprise compounds which can be obtained by reacting

- a) an adduct of an essentially equivalent amount of a diisocyanate with a mixture of a dihydroxyl- or trihydroxyl-terminated polyether or polyester and less than 1 mol %, based on the hydroxyl-terminated prepolymer, of a short-chain diol or triol, and
- b) an amount of a monophenol essentially equivalent to the NCO content.

In another preferred embodiment, the preparation of the component a2) is carried out using an amino-terminated polyalkylene ether which is reacted in the absence of a chain extender with an amount of diisocyanate which is equivalent to, or in excess of, the NH₂ content or with phosgene; the resultant polyisocyanate is then capped with a monophenol IVa, affording a compound of the formula XI



in which R¹⁵ and m are as defined above, t is 0 or 1, R¹⁸ is the divalent radical of an aliphatic, cycloaliphatic, aromatic or araliphatic diisocyanate after removal of the isocyanate groups and R¹⁹ is the m-valent

radical of an amino-terminated polyalkylene ether after removal of the terminal NH_2 groups.

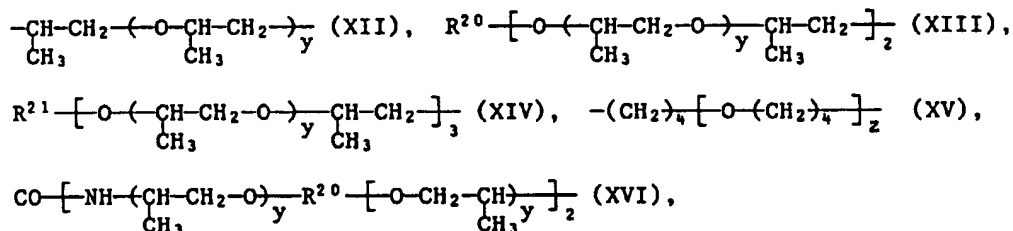
Compositions which contain compounds of the formula XI as the component B) are preferred.

Particularly preferred compositions contain compounds of the formula XI as the component B), in which m is 2 or 3, $-\text{O}-\text{R}^{15}$ is a radical of the formula V or VI, R^{18} is derived from an aliphatic, cycloaliphatic or aromatic diisocyanate and R^{19} is a divalent or trivalent radical of an amino-terminated polyalkylene ether having a molecular weight of 150 to 10,000 after removal of the terminal amino groups.

Most particularly preferred compositions contain as the component B) compounds of the formula XI, in which m is 2, $-\text{O}-\text{R}^{15}$ is a radical of the formula V, t is 0, and R^{19} is derived from a divalent amino-terminated polyalkylene ether having a molecular weight of 500 to 6000.

Most particularly preferred compositions contain as the component B) compounds of the formula XI, in which t is 1, m is 2, $-\text{O}-\text{R}^{15}$ is a radical of the formula V, R^{18} is the divalent radical of an aliphatic or cycloaliphatic diisocyanate after removal of the isocyanate groups and R^{19} is derived from a divalent amino-terminated polyalkylene ether having a molecular weight of 500 to 6000.

The particularly preferred components B) of the two types defined last comprise those wherein R^{19} is a structural element of the formulae XII, XIII, XIV, XV or XVI



wherein y is 5 to 90, preferably 10 to 70, z is 10 to 40, R^{20} is a radical of an aliphatic diol after removal of both OH groups and R^{21} is a radical of an aliphatic triol after removal of the three OH groups.

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The compositions according to the invention obtained from A) and B) can be processed with epoxy resins to cured products having the advantageous properties described above.

Accordingly, the invention also relates to compositions comprising the components A) and B), as defined above, and C), an epoxy resin having at least two 1,2-epoxide groups per molecule; or comprising an adduct of the component A) and an epoxy resin, as well as the component B) and optionally the component C); or comprising the component A), an adduct of a free mercapto terminal groups containing component B) and an epoxy resin and optionally the component C); or comprising an adduct of the component A) and an epoxy resin, an adduct of a free mercapto terminal groups containing component B) and an epoxy resin and optionally the component C).

The preparation of the compositions according to the invention may be carried out in conventional manner by mixing the components with the aid of known mixing equipment, such as stirrers, kneaders or roller mills.

In principle any compound which is customary in the art of epoxy resins may be used as the component C) or for the preparation of the adducts.

Examples of epoxy resins are:

I) Polyglycidyl esters and poly(β -methylglycidyl) esters obtainable by reacting a compound having at least two carboxyl groups in the molecule with epichlorohydrin or β -methylepichlorohydrin. The reaction is expediently carried out in the presence of bases.

Aliphatic polycarboxylic acids may be used as the compound having at least two carboxyl groups in the molecule. Examples of these polycarboxylic acids are oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid or dimerized or trimerized linoleic acid.

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However, it is also possible to use cycloaliphatic polycarboxylic acids, for example tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid.

Aromatic polycarboxylic acids, for example phthalic acid, isophthalic acid or terephthalic acid, may be also used.

II) Polyglycidyl or poly(β -methylglycidyl) ethers obtainable by reacting a compound having at least two free alcoholic hydroxyl groups and/or phenolic hydroxyl groups and a suitably substituted epichlorohydrin under alkaline conditions or in the presence of an acid catalyst, and subsequent treatment with alkali.

Ethers of this type are derived, for example, from acyclic alcohols such as ethylene glycol, diethylene glycol and higher poly(oxyethylene) glycols, propane-1,2-diol or poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol and polyepichlorohydrins.

However, they may be also derived, for example from cycloaliphatic alcohols such as 1,4-cyclohexanedimethanol, bis(4-hydroxycyclohexyl)-methane or 2,2-bis(4-hydroxycyclohexyl)propane, or they may have aromatic nuclei such as N,N-bis(2-hydroxyethyl)aniline or p,p'-bis(2-hydroxyethyl-amino)diphenylmethane.

The epoxide compounds may be also derived from mononuclear phenols, for example from resorcinol or hydroquinone; or they are based on polynuclear phenols, for example bis(4-hydroxyphenyl)methane, 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-propane, or from novolaks obtainable by condensing aldehydes such as formaldehyde, acetaldehyde, chloral or furfuraldehyde with phenols such as phenol, or with phenols which are substituted in the nucleus by

chlorine atoms or by C₁-C₉alkyl groups, for example 4-chlorophenol, 2-methylphenol or 4-tert-butylphenol, or by condensing with bisphenols as described above.

III) Poly(N-glycidyl) compounds obtainable by dehydrochlorination of the reaction products of epichlorohydrin with amines containing at least two amino hydrogen atoms. Examples of these amines are aniline, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine or bis(4-methylaminophenyl)-methane.

The poly(N-glycidyl) compounds comprise, however, also triglycidyl isocyanurate, N,N'-diglycidyl derivatives of cycloalkylene ureas such as ethylene urea or 1,3-propylene urea, and diglycidyl derivatives of hydantoins such as 5,5-dimethylhydantoin.

IV) Poly(S-glycidyl) compounds, for example di-S-glycidyl derivatives which are derived from dithiols, for example ethane-1,2-dithiol or bis-(4-mercaptomethylphenyl) ether.

V) Cycloaliphatic epoxy resins, for example bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether, 1,2-bis(2,3-epoxycyclopentyl-oxy)ethane or 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane-carboxylate.

However, it is also possible to employ epoxy resins in which the 1,2-epoxide groups are linked to different hetero atoms or functional groups; these compounds comprise, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the glycidyl ether/glycidyl ester of salicylic acid, N-glycidyl-N'-(2-glycidyloxypropyl)-5,5-dimethylhydantoin or 2-glycidyloxy-1,3-bis(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

Particularly preferred epoxy resins are polyglycidyl ethers of bisphenols, for example 2,2-bis(4-hydroxyphenyl)propane or bis(4-hydroxyphenyl)methane, those of novolaks formed by the reaction of

formaldehyde with a phenol, or those of the aliphatic diols mentioned above, in particular of butane-1,4-diol, as well as adducts of bisphenol A and glycidylized aliphatic diols.

The curable compositions according to the invention usually contain also additional curing agents D) known to the person skilled in the art, if desired in combination with an accelerator E).

Examples of curing agents D) are aliphatic, cycloaliphatic, aromatic and heterocyclic amines such as bis(4-aminophenyl)methane, aniline-formaldehyde resins, bis(4-aminophenyl)sulfone, propane-1,3-diamine, hexamethylenediamine, diethylenetriamine, triethylenetetramine, 2,2,4-trimethylhexane-1,6-diamine, m-xylylenediamine, bis(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane and 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophoronediamine); polyaminoamides, for example those obtained from aliphatic polyamines and dimerized or trimerized fatty acids; polyphenols such as resorcinol, hydroquinone, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and phenol-aldehyde resins; polythiols, such as polythiols commercially obtainable under the tradename "Thiokols®"; polycarboxylic acids and their anhydrides, for example phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, hexachloroendomethylenetetrahydrophthalic anhydride, pyromellithic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, the acids of the aforementioned anhydrides as well as isophthalic acid and terephthalic acid. Catalytically acting curing agents may be also used; examples of these are tertiary amines [for example 2,4,6-tris(dimethylaminoethyl)phenol]; imidazoles or Mannich bases; alkali metal alcoholates (for example the sodium alcoholate of 2,4-dihydroxy-3-hydroxymethylpentane); tin salts of alkanolic acids (for example tin octanoate); Friedel-Crafts catalysts, such as boron trifluoride and boron trichloride and their complexes and chelates which are obtained by reacting boron trifluoride with, for example, 1,3-diketones; also amidines, preferably dicyanodiamide.

Examples of the accelerator E) are tertiary amines, their salts or quaternary ammonium compounds, such as benzyldimethylamine, 2,4,6-tris-(dimethylaminomethyl)phenol, 1-methylimidazole, 2-ethyl-4-methylimidazole, 4-aminopyridine, triphenylammonium phenolate or tetramethylammonium chloride; or alkali metal alcoholates, such as the sodium alcoholates of 2,4-dihydroxy-3-hydroxymethylpentane; or substituted ureas, such as N-(4-chlorophenyl)-N'N'-dimethylurea or N-(3-chloro-4-methylphenyl)-N'N'-dimethylurea (chlorotoluron).

The properties of the cured end products may be varied depending on the amounts of the components A) and B).

The percentages below refer in each case to the total weight of the components A), B) and C).

If products are required having high strength, high glass transition temperature, high peel strength, high impact strength and high resistance to crack propagation (fracture toughness), the amount of the components A) and B) should in general not exceed 60 % by weight. Such systems are usually heterogeneous. The lower limit depends on the properties required, for example the peel strength. In general the components A) and B) should amount to more than 5 % by weight, preferably more than 10 % by weight.

If on the other hand products are required having as high a flexibility as possible, at least 40 % by weight, preferably more than 60 % by weight, of the components A) and B) should be present.

If the component A) and/or B) has been modified by adduct formation with an epoxy resin, then a separate component C) is not necessarily required.

To obtain a highly flexible system, the component A) is modified preferably by adduct formation with epoxy resins; adducts of liquid acrylonitrile-butadiene copolymers having groups reactive toward epoxy resins with glycidyl ethers of aliphatic diols, such as 1,4-butanediol or 1,6-hexanediol, are particularly preferred.

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The weight ratio of A) to B) can be varied within a wide range. Preferred range of A) to B) is 50:1 to 1:50, 20:1 to 1:10 being particularly preferred, 5:1 to 1:5 being most particularly preferred.

The proportion of the epoxy resin C) in the total amount of A), B) and C) may be likewise varied within a wide range. To obtain cured products with an increased flexibility, smaller amounts of C), for example 10 to 30 % by weight, are generally used, where the component C) may be also present as an adduct of A), while to obtain cured products with a high strength greater amounts of C), for example 50 to 95 % by weight, preferably 60-80 % by weight, are generally used.

The amount of the curing agent D) and the accelerator E) generally depends on the type of curing agent and is chosen by a person skilled in the art in a manner known per se.

Heat-curable systems containing the component A), B) and C) in combination with primary and/or secondary aromatic amines or with amidines as the curing agent D), are preferred.

Dicyanodiamide is a particularly preferred curing agent. In this case 0.1-0.5 mol of the curing agent is preferably used per one mol of epoxide groups.

The curing of the compositions according to the invention may be performed at lower temperatures or at higher temperatures. Curing temperatures above 80°C are preferred.

In the heat-curing process the curing temperatures are generally between 80 and 250°C, preferably between 100 and 180°C. If desired, curing can be also performed in two stages, for example by interrupting the curing process, or, where a curing agent for a higher temperature is used, the curable mixture is allowed partly to cure at lower temperatures. The

products obtained in this manner are still fusible and soluble pre-condensates (so-called "B stage resins") and are suitable, for example, for moulding compounds, sintered powders or prepregs.

Reactive thinners, for example styrene oxide, butyl glycidyl ether, 2,2,4-trimethylpentyl glycidyl ether, phenyl glycidyl ether, cresyl glycidyl ether or glycidyl esters of synthetic, highly branched, mainly tertiary aliphatic monocarboxylic acids, may be added to the curable mixtures, if desired, to lower further the viscosity.

The mixtures according to the invention may also comprise, as further customary additives, plasticizers, extenders, fillers and reinforcing agents, for example coal tar, bitumen, textile fibres, glass fibres, asbestos fibres, boron fibres, carbon fibres, mineral silicates, mica, quartz powder, aluminium hydroxide, bentonite, kaolin, silica aerogel or metal powders, for example aluminium powder or iron powder, also pigments and colourants, such as carbon black, oxide dyes and titanium dioxide, flame retardants, thixotropic agents, flow control agents, such as silicones, waxes and stearates which are to some extent also employed as mould release agents, tackifiers, antioxidants and light shielding agents.

The cured products are distinguished by the advantageous properties outlined at the outset.

The invention accordingly also relates to the products obtainable by curing the compositions comprising A), B) and C), in which case the components A) and/or B) may be also used as adducts with epoxy resins.

The mixtures according to the invention may be employed, for example, as adhesives, adhesive tapes, patches, matrix resins, paints or sealants or generally for the production of cured products. They may be used in a formulation adapted in each case to the special application field, with or without filler, for example as coating agents, coating compounds, paints, moulding compounds, dip resins, casting resins, impregnating resins, laminating resins, matrix resins and adhesives.

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The invention also relates to the use of the mixtures according to the invention for the above purposes.

In the examples below which elucidate the invention, the parts are parts by weight, unless otherwise stated.

Examples 1 to 8:

A. Preparation and testing of adhesive formulations

General procedure:

The mixtures described in Table I and containing the prepolymers described in part B, are prepared in a triple-roll mill and are used to join degreased, sand-blasted, 1.5 mm thick aluminium panels and degreased 1.5 mm thick steel panels, the test specimens being cured for 30 minutes at 180°C with a 2.5 x 1.25 cm² overlap. The lap shear strength (N/mm²) is determined on the substrates.

The T-peel strength is measured on 0.8 mm thick degreased steel panels, curing being effected for 1 hour at 180°C using the same mixture.

The glass transition temperature (T_g) is determined by dynamic-mechanical spectroscopy (using the Du Pont 9000 thermal analysis instrument) on a glass fibre prepreg, impregnated by the above mixture and cured for 1 hour at 180°C.

B. Preparation of prepolymers

Prepolymer 1A

730 g of bisphenol A diglycidyl ether (epoxide content 5.4 equivalents/kg), 200 g of carboxyl-terminated acrylonitrile/butadiene copolymer (acrylonitrile content 26 %, acid value 32 mg of KOH/g), 64 g of bisphenol A and 5 g of triphenylphosphine are heated for 3 hours at 130°C in a flat flange flask provided with a stirrer, nitrogen inlet and reflux condenser, until a viscous epoxy resin having an epoxide content of 3.3 equivalents/kg with an Epprecht viscosity of 130,000 mPas (40°C) has formed.

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Prepolymer 1B

A mixture of 354 g of dry dihydroxyl-terminated polypropylene glycol (MW = 2000), 1.8 g of trimethylolpropane and 0.1 ml of dibutyltin dilaurate is added to 88.8 g of isophorone diisocyanate in the course of one hour at 100°C under nitrogen. Stirring is continued for 2 hours at 100°C, after which 48 g of p-cresol are added and stirring is continued for a further 3 hours at 100°C until free isocyanate is no longer detectable. A viscous resin is obtained with the following analysis:
Epprecht viscosity: 120,320 mPas (25°C),
 $M_n = 2750$, $M_w/M_n = 2.3$ (GPC).

Prepolymer 2

A mixture of 354 g of dry dihydroxyl-terminated polypropylene glycol (MW = 2000) and 0.1 ml of dibutyltin dilaurate is added to 54.4 g of hexamethylene diisocyanate in the course of 1 hour at 60°C under nitrogen. 1.8 g of trimethylolpropane is then added, and the reaction mixture is stirred for 1 hour at 100°C until an isocyanate content of 2.7 % is reached, and is then allowed to react with 31.1 g of p-cresol for 3 hours at 100°C until free isocyanate is no longer detectable. A viscous resin is obtained with the following analysis:
Epprecht viscosity: 133,120 mPas (25°C);
molecular weight (GPC): $M_n = 4660$ ($M_w/M_n = 3.5$).

Prepolymer 3

A mixture of 354 g of dry dihydroxyl-terminated polypropylene glycol and 0.1 ml of dibutyltin dilaurate is added to 56.3 g of a mixture of toluylene diisocyanate isomers in the course of 1 hour at 100°C under nitrogen, 1.8 g of trimethylolpropane is added and the reaction mixture is stirred for 1 hour at 100°C until an isocyanate content of 2.6 % is reached. 30 g of p-cresol are then added, the mixture is stirred for 3 hours at 100°C until free isocyanate is no longer detectable and a viscous resin with the following analysis is isolated:
Epprecht viscosity: 184,320 mPas (25°C);
molecular weight (GPC): $M_n = 2850$, $M_w/M_n = 5.6$.

Prepolymer 4

354 g of dry dihydroxyl-terminated polytetrahydrofuran (MW = 2000) containing 0.1 ml of dibutyltin dilaurate are added to 54.4 g of hexamethylene diisocyanate in the course of 1 hour at 100°C under nitrogen, 1.8 g of trimethylolpropane is added and the mixture is stirred for a further one hour at 100°C until an isocyanate content of 2.8 % is reached. The mixture is then allowed to react with 32.3 g of p-cresol for 3 hours at 100°C until free isocyanate is no longer detectable, affording a viscous resin with the following analysis:

Epprecht viscosity: 14,080 mPas (80°C);

molecular weight (GPC): $M_n = 2200$, $M_w/M_n = 9.9$.

Prepolymer 5

354 g of dry dihydroxyl-terminated polypropylene glycol (MW = 2000) containing 0.1 ml of dibutyltin dilaurate are added to 54.4 g of hexamethylene diisocyanate in the course of 1 hour at 100°C under nitrogen, 1.8 g of trimethylolpropane is then added and the reaction mixture is stirred for one hour until an isocyanate content of 2.6 % is reached. The mixture is then allowed to react with 34.4 g of hydroquinone monomethyl ether for 3 hours at 100°C until free isocyanate is no longer detectable, affording a viscous resin with the following analysis:

Epprecht viscosity: 60,160 mPas (25°C);

molecular weight (GPC): $M_n = 4840$, $M_w/M_n = 3.3$.

Prepolymer 6

A mixture of 354 g of dihydroxyl-terminated polypropylene glycol (MW = 2000), 1.8 g of trimethylolpropane and 0.1 ml of dibutyltin dilaurate is added to 88.1 g of isophorone diisocyanate in the course of 1 hour at 100°C under nitrogen with stirring. The reaction mixture is stirred for 2 hours at 100°C, after which 32 g of mercaptoethanol are added and stirring is continued for 20 hours at 100°C until free isocyanate is no longer detectable. A viscous resin is obtained with the following analysis:

Epprecht viscosity: 204,800 mPas (25°C);

molecular weight (GPC): $M_n = 1690$, $M_w/M_n = 6.7$.

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Prepolymer 7

A mixture of 105 g of prepolymer 6 and 130 g of a tetraglycidyl ether of 2,2,6,6-tetrahydroxymethylcyclohexan-1-ol (epoxide content 7.4 equivalents/kg) is heated for four hours at 60°C, affording an epoxy resin with the following analysis:

epoxide content: 4.1 equivalents/kg;

Epprecht viscosity: 10,560 mPas (80°C).

Prepolymer 8

A mixture of 105 g of prepolymer 6 and 70 g of a bisphenol A diglycidyl ether (epoxide content 5.4 equivalents/kg) is heated for four hours at 60°C, affording an epoxy resin with the following analysis:

epoxide content: 2.2 equivalents/kg;

Epprecht viscosity: 174,080 mPas (25°C).

Prepolymer 9

A mixture of 354 g of dihydroxyl-terminated polypropylene glycol (MW = 2000), 1.8 g of trimethylolpropane and 0.1 ml of dibutyltin dilaurate is added to 54.4 g of hexamethylene diisocyanate in the course of one hour at 100°C under nitrogen and the reaction mixture is stirred for a further 2 hours until a prepolymer having 2.4 % of free isocyanate content is formed. 32 g of caprolactam are then added and stirring is continued for 3 hours at 100°C until free isocyanate is no longer detectable. A viscous resin with the following analysis is obtained:

Epprecht viscosity: 19,200 mPas (25°C).

Prepolymer 10

A mixture of 354 g of dihydroxyl-terminated polytetrahydrofuran (MW = 2000), 1.8 trimethylolpropane and 0.1 ml of dibutyltin dilaurate is added to 88.8 g of isophorone diisocyanate in the course of one hour at 100°C under nitrogen and the reaction mixture is stirred for a further two hours. 32 g of caprolactam are then added and stirring is continued for 3 hours until free isocyanate is no longer detectable. 460 g of a viscous resin with the following analysis are obtained:

Epprecht viscosity: 28,160 mPas (40°C).

Prepolymer 11

A mixture of 200 g of diamino-terminated polypropylene glycol having a molecular weight of 2000 (Jeffamine® D2000 from Texaco) and 23.7 g of p-cresol is added to 33.6 g of hexamethylene diisocyanate in the course of 30 minutes under nitrogen. The reaction mixture is then heated to 100°C, 0.1 ml of dibutyltin dilaurate is added and the mixture is stirred for 3 hours at 100°C. A viscous isocyanate-free resin with the following analysis is obtained:

Epprecht viscosity: $\eta_{25} = 420,000$ mPas;

molecular weight (GPC): $M_n = 1800$, $M_w/M_n = 9.0$.

Prepolymer 12

A mixture of 354 g of dry dihydroxyl-terminated polypropylene glycol ($M_n = 2000$) and 0.3 ml of dibutyltin dilaurate is added to 54.4 g of hexamethylene diisocyanate in the course of 1 hour at 100°C under nitrogen. 1.8 g of trimethylolpropane is added, after which the reaction mixture is stirred for 3 hours at 100°C until an isocyanate content of 2.2 % is reached; 120 g of cashew nut oil (phenol content 3.4 equivalents/kg) are then added at 100°C and stirring is continued for a further 3 hours at 100°C until a viscous isocyanate-free resin with the following analysis is formed:

viscosity $\eta_{25} = 33,280$ mPas.

Prepolymer 13

A mixture of 50 g of hydroxyl-terminated polybutadiene (ARCO RD 45 HT) and 0.1 ml of dibutyltin dilaurate are added to 88 g of isophorone diisocyanate in the course of 1 hour at 100°C under nitrogen with stirring; the reaction mixture is stirred at 100°C for 1 hour, after which 250 g of dry dihydroxyl-terminated polybutylene glycol ($M_n = 2000$) are added in the course of 1 hour and stirring is continued for 2 hours. 23.8 g of hydroquinone monomethyl ether are added to this isocyanate-containing prepolymer and the mixture is stirred for 3 hours at 100°C. A viscous isocyanate-free resin with the following analysis is obtained:

Epprecht viscosity: $\eta_{40} = 207,360$ mPas;

molecular weight (GPC): $M_n = 3370$, $M_w/M_n = 6.2$.

C. Formulation and testing of adhesives

The results of the tests described under A and the composition of the adhesives are given in the following Table I.

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Table I

Example No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Diglycidyl ether based on bisphenol A (epoxide content 5.4 equivalents/kg)(g)	70	70	70	70	70	70	70	70	70	70	70	70	35
Butanediol diglycid ether (epoxide content 9.2 equivalents/kg) (g)	5	5	5	5	5	5	5	5	5	5	5	5	2.5
Glycidyloxypropyl trimethoxysilane (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-
Wollastonite P1 (g)	30	30	30	30	30	30	30	30	30	30	30	30	15
Dicyanodiamide (g)	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	4.9
Chlorotoluron (g)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.25
Pyroge silica (g)	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	3.5
Adduct 1A	30	30	30	30	30	30	30	30	30	30	30	30	15
Prepolymer No.	1B	2	3	4	5	6	7	8	9	10	11	12	13
Prepolymer (g)	30	30	30	30	30	30	30	30	30	30	30	30	15
Lap shear strength on Al (N/mm ²)	25.1	27.8	21.0	28.0	27.8	23.6	26.0	25.1	21.9	22.7	28.2	29.1	31.3
Lap shear strength on steel (N/mm ²)	24.1	21.6	19.0	20.9	22.1	22.6	27.6	23.7	13.9	24.7	21.6	23.6	26.2
T-peel on degreased steel (N/mm)	2.4	6.0	3.0	6.1	6.2	4.6	7.1	4.5	2.1	2.8	7.6	8.0	6.4
Fracture (% cohesion fraction)	40	50	50	50	50	50	100	30	10	10	100	90	n.d.
Glass transition temperature*) (°C)	63	n.d.	n.d.	n.d.	n.d.	78	93	83	n.d.	n.d.	n.d.	n.d.	n.d.

*) n.d. = not determined

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A composition comprising

A) a liquid copolymer based on butadiene and a polar, ethylenically unsaturated comonomer or a liquid copolymer based on butadiene, a polar, ethylenically unsaturated comonomer and a further non-polar ethylenically unsaturated comonomer, or an adduct of said liquid copolymer with an epoxy resin via terminal groups of said copolymer reactive toward epoxy resins, and

B) a compound of the formula I



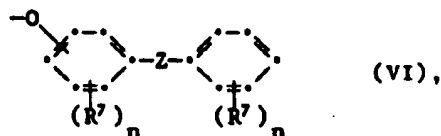
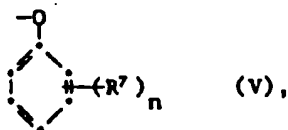
in which m is 2 to 6, R^1 is the m-valent radical of an elastomeric prepolymer after removal of the terminal isocyanate, amino or hydroxyl groups, which is soluble or dispersible in epoxy resins, X is -O- or -NR²-, where R² is hydrogen, C₁-C₆alkyl or phenyl, Y is -O-, R³ is the radical of a monophenol or of an aliphatic or cycloaliphatic mercaptoalcohol after removal of one hydroxyl group, or Y and R³ form jointly the radical of an aliphatic lactam which is attached to the carbonyl group via the N atom, with the proviso that at least one of the groups -X- or -Y-R³ contain a nitrogen atom.

2. A composition according to claim 1, in which said liquid copolymer contains terminal groups reactive towards epoxy resins.

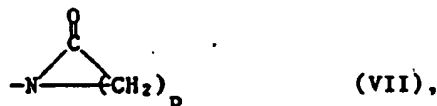
3. A composition according to claim 1, in which the component A) is a liquid butadiene-acrylonitrile copolymer.

4. A composition according to claim 1, in which the component A) is used as adduct of a butadiene-acrylonitrile copolymer having functional groups reactive toward epoxy resins with an epoxy resin.

5. A composition according to claim 1 in which $-Y-R^3$ is a radical of the formula V or VI



in which R^7 is C_1-C_{20} alkyl, C_1-C_{20} alkoxy, C_2-C_{20} alkenyl, C_2-C_6 alkynyl, $-CO-OR^8$ or halogen, n is 0, 1 or 2, Z is a direct C-C bond or a bridge selected from the group consisting of $-CR^9R^{10}-$, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-COO-$, $-CONR^{11}-$ and $-SiR^{12}R^{13}-$, R^9 , R^{10} and R^{11} independently of one another are hydrogen, $-CF_3$ or C_1-C_6 alkyl, or R^{10} and R^{11} form jointly with the carbon atom they have in common a cycloaliphatic radical having 5 to 12 carbon atoms, R^8 is C_1-C_{20} alkyl and R^{12} and R^{13} are C_1-C_6 alkyl; or in which $-Y-R^3$ is a radical of the formula VII



in which p is 3 to 5; or in which $-Y-R^3$ is a radical of the formula VIII



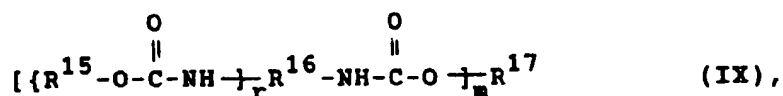
in which R^{14} is C_2-C_{12} alkylene or cycloalkylene having 5 to 7 cyclic carbon atoms.

6. A composition according to claim 1, in which X is $-NH-$ and Y is $-O-$.

7. A composition according to claim 1, in which the component B) is a compound of the formula I as defined in claim 1 which can be obtained by reacting
- a prepolymeric polyisocyanate which
 - is an adduct of a polyisocyanate with a prepolymeric polyhydroxyl or polysulfhydryl compound or with a mixture of such compounds, or is an adduct of a polyisocyanate with a prepolymeric polyhydroxyl or polysulfhydryl compound or with a mixture of such compounds in combination with a chain extender, or
 - is derived from a prepolymeric polyether amine, with
 - at least one monophenol.

B.

8. A composition according to claim 7, in which the component a1) is an adduct of a polyisocyanate with a hydroxyl-terminated polyether.
9. A composition according to claim 7, in which the component a1) is prepared from a mixture of hydroxyl-terminated polybutadiene and a hydroxyl-terminated polyalkylene glycol or a hydroxyl-terminated polyalkylene glycol with grafted 1-olefins.
10. A composition according to claim 7, in which the component b) is a mixture of a monophenol with a small amount of a bisphenol.
11. A composition according to claim 1 containing as the component b) compounds of the formula IX



in which R^{15} is the radical of a monophenol after removal of the phenolic hydroxyl group, r is an integer between 1 and 3, R^{16} is the $r+1$ -valent radical of an aliphatic, cycloaliphatic, aromatic or araliphatic polyisocyanate after removal of the isocyanate groups, m is as defined in claim 1, R^{17} is a m -valent hydroxyl-terminated polyester or polyether radical after removal of the terminal OH groups, with the proviso that the radicals R^{15} and R^{16} may be different within a given molecule.

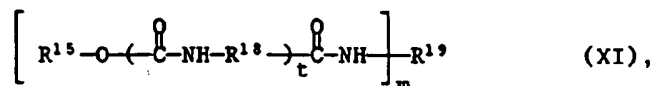
12. A composition according to claim 11, in which m is 2 or 3, r is 1, $-O-R^{15}$ is a radical of the formula V according to claim 4, R^{16} is derived from an aliphatic or cycloaliphatic diisocyanate and R^{17} is a divalent or trivalent radical of a polyalkylene ether polyol having a molecular weight of 150 to 3000 after removal of the terminal hydroxyl groups.

13. A composition according to claim 7, in which the component B) can be obtained by reacting
a1) an adduct of an essentially equivalent amount of a diisocyanate with

a mixture of a dihydroxyl- or trihydroxyl-terminated polyether or polyester and less than 1 mol %, based on the hydroxyl-terminated prepolymer, of a short-chain diol or triol, and

b) an amount of a monophenol essentially equivalent to the NCO content.

14. A composition according to claim 1 containing as the component B) a compound of the formula XI



in which R^{15} and m are as defined in claim 10, t is 0 or 1, R^{18} is the divalent radical of an aliphatic, cycloaliphatic, aromatic or araliphatic diisocyanate after removal of the isocyanate groups and R^{19} is the m -valent radical of an amino-terminated polyalkylene ether after removal of the terminal NH_2 groups.

15. A composition comprising the components A) and B) according to claim 1, and C), an epoxy resin having at least two 1,2-epoxide groups per molecule; or comprising an adduct of the component A) and an epoxy resin, as well as the component B); or comprising an adduct of the component A) and an epoxy resin, component B and component C); or comprising the component A) and an adduct of a free mercapto terminal groups containing component B) and an epoxy resin; or comprising the component A), an adduct of a free mercapto terminal groups containing component B) and an epoxy resin and component C); or comprising an adduct of the component A) and an epoxy resin, and an adduct of a free mercapto terminal groups containing component B) and an epoxy resin; or comprising an adduct of the component A) and an epoxy resin, an adduct of a free mercapto terminal groups containing component B) and an epoxy resin and component C).

16. A composition according to claim 15, in which the component C) is a polyglycidyl ether of a bisphenol, a novolak or an aliphatic diol or is an adduct of bisphenol A and glycidylized aliphatic diols.

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17. A process for the preparation of crosslinked products characterized by curing a composition according to claim 15 by means of a curing agent D) which is active at room temperature or at elevated temperature or by means of an epoxy curing agent D) combined with an accelerator E).

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K-16987/+

Modified epoxy resins

07 MARS 1995

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Abstract

Compositions are described which contain A) a liquid copolymer based on butadiene, a polar, ethylenically unsaturated comonomer and optional a further ethylenically unsaturated comonomer, and B) a compound of the formula I



in which m is 2 to 6, R^1 is the m-valent radical of an elastomeric prepolymer after removal of the terminal isocyanate, amino or hydroxyl groups, which is soluble or dispersible in epoxy resins, X is -O- or -NR²-, where R² is hydrogen, C₁-C₆alkyl or phenyl, Y is -O-, R³ is the radical of a monophenol or of an aliphatic or cycloaliphatic mercaptoalcohol after removal of one hydroxyl group, or Y and R³ form jointly the radical of an aliphatic lactam which is attached to the carbonyl group via the N atom, with the proviso that at least one of the groups -X- or -Y-R³ contain a nitrogen atom.

The compositions may be used to render epoxy resins more flexible.